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Characterisation of coloured TiO_x/Ti/glass systems

Ł. Skowroński[a,*], M. Trzcinski[a], A.J. Antończak[b], P. Domanowski[c], M. Kustra[a], W. Wachowiak[a], M.K. Naparty[a], T. Hiller[a], A. Bukaluk[a], A.A. Wronkowska[a]

[a] Institute of Mathematics and Physics, University of Technology and Life Sciences, Kaliskiego 7, 85-789 Bydgoszcz, Poland
[b] Laser and Electronic Fiber Group, Department of Electronics, Wroclaw University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wroclaw, Poland
[c] Faculty of Mechanical Engineering, University of Technology and Life Sciences, Kaliskiego 7, 85-789 Bydgoszcz, Poland

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ABSTRACT

This paper presents a study of the optical properties, microstructure and chemical composition of titanium oxide layers deposited on Ti film using gas injection magnetron sputtering (GIMS). The samples are examined by means of spectroscopic ellipsometry, atomic force microscopy and X-ray photoelectron spectroscopy. The investigation is complemented by colorimetric measurements. The influence of deposition time on the thickness of dielectric layers has been found. A comprehensive analysis of effective dielectric functions of titanium and titanium oxide films is presented. The thickness of titanium oxide film ranges from 13 nm to 54 nm and directly determines the colour of a sample from gold to blue, respectively.

1. Introduction

Titanium and titanium oxides have been extensively developed for many years because they demonstrate excellent mechanical properties and are cheap, non-toxic, biocompatible and chemically stable [1]. Titanium and its alloys are used in aircraft, naval ships and the spacecraft industry due to their strength to density ratio, high corrosion and fatigue resistance [2]. Titanium oxides are used as white pigment in paints and some high-tech applications including electrochromic devices [3] and dye-sensitized solar cells (DSSC) [4,5]. Furthermore, their doped forms can be employed as photocatalysts [6] and antireflection coatings [7]. Moreover, due to expressive colours of titanium oxides and oxynitrides deposited on metal, these compounds can be applied as a decorative material for architecture, the automotive industry, electronics and jewellery [8,9].

Magnetron sputtering is a surface coating technique, which can be used in many applications. The method is widely employed in the industry to produce different types of coatings, also on large-sized elements. One of the recently developed types of physical vapour deposition (PVD) methods is gas injection magnetron sputtering (GIMS) [10,11].

Previous studies on colours of titanium oxide layers were concerned with the optical properties, microstructure, chemical composition and visual aspects of coatings prepared mostly by anodic oxidation [12,13] and laser-induced titanium dioxide on titanium plate [14,15]. The aim of this work is the study of optical properties and the microstructure of the titanium oxide layer and titanium undercoat formed by the GIMS method and its impact on a colour of samples. In this paper we present a technological process by which one can obtain colour layers, e.g. for architectural glazing.

2. Experimental details

2.1. Sample preparation

To obtain the interference colours of TiO_2 layers, the Ti undercoat was deposited directly on the float glass. The Ti and TiO_2 films were deposited by means of magnetron sputtering (GIMS), using a commercial production line in the Bohamet company [16]. The substrate (float glass 5 mm) was degreased using a commercial solution based on a mixture of alcohols and surfactants. The plasma cleaning of the substrates was performed just before the deposition process. A pressure in the vacuum chamber before the deposition was set at 0.01 Pa. The substrate was not intentionally heated.

To produce titanium and titanium oxide films, the three Ti rectangular targets (at a purity of 99.5%) were applied. Each target is powered using a 30 kW power supply. The following technological parameters were kept during the production of the Ti undercoat:

* Corresponding author. Tel.: +48 792503618.
E-mail address: lukasz.skowronski@utp.edu.pl (Ł. Skowroński).

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0169-4332/

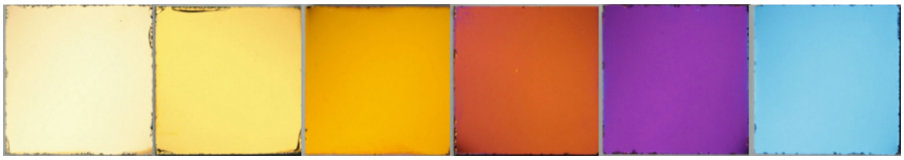

Fig. 1. The photo of produced TiO_2/Ti/glass samples (from left to right): gold, yellow, orange, red, purple and blue. (For check the color of samples, the reader is referred to the web version of this article.)

the pressure was 0.16 Pa (the Ar was used as a sputter gas) and the time of deposition was 538 s.

The TiO_2 layers were obtained using the same targets as mentioned above. The deposition was performed in an Ar/O_2 atmosphere at a pressure of 0.25 Pa. The ratio of reactive gas (O_2) to inert gas (Ar) flow was 4:1. Different thicknesses of titanium oxide films and colours of sample were obtained, changing the time of deposition from about 270 s to 1120 s.

2.2. Measurements

The complex dielectric function $\widetilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ of the obtained titanium and titanium oxide layers and thickness of dielectric films have been determined using spectroscopic ellipsometry (SE) in the wavelength range from 193 nm to 20,000 nm (6.5–0.062 eV). The ellipsometric parameters Ψ and Δ were measured for three angles of incidence (65°, 70° and 75°) by two instruments: the V-VASE from J. A. Woollam Co., Inc. and a FTIR spectroscopic ellipsometer Sendira from Sentech Instruments GmbH. The spectral ranges of the devices are: 193–2200 nm (6.5–0.58 eV) and 1540–20,000 nm (0.8–0.062 eV) for V-VASE and Sendira, respectively. The thickness of the opaque Ti undercoat was determined using a confocal optical microscope Lext OLS 4000 from Olympus.

The surface topography of titanium and titanium oxide films was examined by an atomic force microscope (AFM) Innova from Bruker. The imaging contact mode with a scan size of 2 μm × 2 μm and standard Si tips was used to perform the surface characterisation. The roughness parameters R_a and R_q were determined by the use of the NanoScope Analysis software (version 1.40). The R_a and R_q are defined as:

$$R_a = \frac{1}{N}\sum_{j=1}^{N}|Z_j|, \tag{1}$$

$$R_q = \sqrt{\frac{\sum_{j=1}^{N} Z_j}{N}}. \tag{2}$$

In Eqs. (1) and (2) the quantities Z_j and N are the current surface height value and number of measured points, respectively.

X-ray photoelectron spectroscopy (XPS) measurements were performed in a UHV chamber with a base pressure $<2\times10^{-8}$ Pa equipped with a VG Scienta R3000 photoelectron spectrometer and a monochromatized AlK_α radiation source ($h\nu$ = 1486.6 eV). Photoelectron spectra were taken at an electron analyzer resolution set to ΔE = 200 meV. In order to investigate the composition and chemical state of subsurface layers, the sample was, for several minutes, sputtered by Ar^+ ions of 4 keV energy at the incidence angle of 69° before XPS measurements.

For an objective evaluation of the colour, an optical spectrometer (Avantes type AvaSpec-ULS2048L) was applied. The integrating sphere with an internal light source (Avantes type AvaSphere-50-LS-HAL, T_c = 27.00 K) was simultaneously used as a light source and measuring port. The spectrophotometer was calibrated with two standards: a PTFE diffusion plate (Avantes, WS-2), as well as an Al + MgF_2 reference mirror (Avantes, RS-2, 200–2500 nm). The measurement was performed after stabilization of the working conditions of the light source, which means after approx 10 min. The reflectance spectra were determined in the wavelength range of 360–880 nm with a resolution of 1.2 nm and the averaging time of 1.05 ms. Data processing was performed using the software AvaSoft-full.

3. Results and discussion

The expressive colour of the sample can be obtained on a titanium plate through the preparation of the titanium oxide layer by means of anodic oxidation [12,13] or laser-induced heating [14,15]. In each of the above-mentioned cases the dielectric film is formed on the surface of metal. In this study we show a method of production of coloured coatings using a two-step magnetron sputtering process. At first, the Ti undercoat was deposited, and next – the dielectric oxide layer was grown. Pure TiO_2 films are transparent in the visible spectral range (the fundamental band-gap is about 3.2 eV [17–19]). The observed colour formation is caused by the interference effect. Obviously, for thin titanium oxide layers (tens of nm), the first order of interference of light reflected from the surface of both oxide film and titanium is considered. The photos of samples are presented in Fig. 1. In Table 1 we show a color, the time of deposition and determined thickness of titanium and titanium oxide layers. The first sample in Table 1 is the undercoat and the thickness of titanium dioxide refers to the Ti native oxide. The methods used to determine and analyse the thicknesses of titanium and its oxide are given in Table 1, which will be discussed further on.

The AFM images of the surface of Ti (undercoat) and TiO_2 (a blue sample) films are presented in Fig. 2a and 2b, respectively. The roughness parameters R_a and R_q for the titanium undercoat are 2.01 ± 0.18 nm and 2.68 ± 0.21 nm, respectively. The topography of titanium oxide layers (a representative AFM image for a blue sample is shown in Fig. 2b) is similar to the topography of the titanium surface. This means that during oxide film formation the dielectric layer generally reproduces the morphology of the metallic film. For other samples the roughness parameters are in the range from 2.24 nm to 3.01 nm and from 2.80 nm to 3.78 nm for R_a and R_q, respectively. There is no correlation between these quantities and the time of deposition of the oxide layer.

To obtain the information about the chemical composition, and additionally, about the chemical state of the samples' components, photoelectron spectroscopy (XPS) measurements were performed.

Table 1
An approximate colour of sample, the time of deposition and thickness of titanium and titanium oxide layers.

No.	Colour	Titanium oxide		Titanium (undercoat)	
		t_o (s)	d_o(nm)	t_{Ti} (s)	d_{Ti} (nm)
1.	Grey (metallic)	–	1.34 ± 0.05[a]		
2.	Gold	269	13.16 ± 0.12		
3.	Yellow	407	19.23 ± 0.10		
4.	Orange	537	26.51 ± 0.13	538	315±10
5.	Red	672	32.26 ± 0.08		
6.	Purple	790	37.54 ± 0.09		
7.	Blue	1119	54.72 ± 0.11		

[a] The thickness of native oxide.